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ON CHONDROSAMINE

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Theoretically there are possible as many α -amino hexoses as there exist hexoses, namely, eight in the *d*-series, and as many in the *l* and *dl*-series. Of the eight possible amino-sugars only one has been discovered in nature, namely, glucosamine; this also was prepared synthetically by Fischer and Leuchs,¹ and to it the configuration of glucose was ascribed. More recent investigations have shown that two explanations for the configuration of the sugar are possible: one of glucosamine and the other of mannosamine, and that at present it is not possible to give preference to either one of the two.²

In the course of our investigations on the structure of chondroitin sulphuric acid we isolated an α -amino hexose isomeric with the one previously described. It was named chondrosamine.³ On the basis of further investigation the conclusion was reached that chondrosamine has the configuration of either α -altrosamine or of α -allosamine. The grounds for the conclusion are the following:

1. On oxidation with bromine the amino-hexose was transformed into a tetroxyaminocaproic acid having $[\alpha]_D^{28.5} = -29.23$ (glucosaminic acid has $[\alpha]_D = -14.65^\circ$). On reduction with hydroiodic acid a hydroxyaminocaproic acid was obtained. The properties of this were identical with the acid obtained on reduction of glucosaminic acid. By this was demonstrated that chondrosamine contained a normal carbon chain.

2. On oxidation with nitric acid of the deaminized chondrosaminic acid an anhydrodicarboxylic acid (epichondrosic acid) was obtained. M.P. = 201–202°C., optically inactive. C = 37.58%; H = 4.42% (theory, C = 37.50; H = 4.20).

3. On oxidation with nitric acid directly of the deaminized amino-sugar an acid (chondrosic) was obtained, identical in composition: C = 37.11%; H = 4.15%; but different in properties: M. P. = 179–181°; $[\alpha]_D^{28} = -16.56^\circ$.

4. On heating in a sealed tube at 150° with equal parts of hydrochloric and hydrobromic acid, chondrosic acid was converted into dehydromucic acid: C = 45.84%; H = 3.08% (theory, C = 46.16, H = 2.57).

5. On heating at 200°C., chondrosic acid was converted into pyromucic acid. C = 53.56%; H = 3.57 (theory, C = 53.37, H = 4.14). M.P. = 135°C. Isosaccharic acid is converted into dehydromucic

and into pyromucic acids under the same conditions as chondrosic acid, hence it was concluded that the two acids were similar in their structure, namely, that in both an oxygen bridge existed between the α - and α_1 -carbon atoms.⁴

6. The anhydrodicarboxylic acids (derived from hexoseamines) have as many asymmetric carbon atoms in their molecule as the corresponding acids derived from hexoses. Therefore, there are possible only two optically inactive anhydrodicarboxylic acids: namely, one corresponding to mucic and the other to allomucic acid. This consideration limits the possibilities of configuration of epichondrosic acid to anhydromucic, or anhydroallomucic. The fact that chondrosamine forms a phenyl osazone identical in its properties with that of allose decides the choice between the two configurations in favor of anhydroallomucic.

7. Regarding the configuration of chondrosine the choice remains between that of *l*-allosamine or of *l*-altrosamine. Both anhydroallomucic and anhydrotalomucic acids are obtainable from chondrosamine depending on the procedure in preparation.

It was attempted to prepare chondrosaminic acid synthetically from ribosimine by the action of prussic acid. The acid obtained in this manner had the composition of hexosaminic acid, C = 37.02%, H = 6.58%, and N = 7.44% (theory, C = 36.92, H = 6.66, N = 7.18). M. P. = 198°C., $[\alpha]_D^{25} = -9.4^\circ$. The acid was evidently epimeric with chondrosaminic, and on treatment with nitric acid it should have yielded chondrosic acid. Unfortunately for lack of material this experiment had to be deferred.

¹ Fischer, E., and Leuchs, H., *Berlin, Ber. D. chem. Ges.*, **36**, 24 (1903).

² Irvine, J. C., and Hynd, A., *London, J. Chem. Soc.*, **101**, 1128 (1912); **105**, 698 (1914).

³ Levene, P. A., and La Forge, F. B., *J. Biol. Chem.*, **18**, 123 (1914).

⁴ Fischer, E., and Tiemann, F., *Berlin, Ber. D. chem. Ges.*, **24**, 2139 (1891).

THE FREEZING-POINT-SOLUBILITY LAW FOR IDEAL SOLUTIONS

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When a solution is formed by mixing together two completely miscible pure liquids, it is found that when the two constituents resemble each other very closely the formation of the solution takes place without appreciable heat-effect or volume-change. Such solutions have been termed *ideal solutions*; and experiments have shown that the vapor pres-